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Research article

Kinetics of Acid Orange 7 oxidation by using carbon fiber and reticulated vitreous carbon in an electro-Fenton process

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ABSTRACT

In this study, a micro-scale parallel plate reactor was built to electrochemically generate hydrogen peroxide (H_2O_2) and to develop the Fenton reaction *in situ*, for the treatment of toxic organic pollutants. Two types of carbon materials were compared and used as cathodes: unidirectional carbon fiber (CF) and reticulated vitreous carbon (RVC). As anode, a stainless steel mesh was used. The results of H_2O_2 were experimentally compared by means of electrogeneration process. RVC cathode with dimensions of $2.5 \times 1 \times 5$ cm (170 mA and variable voltage $V = 2.0–2.7$) and 180 min produced 5.3 mM H_2O_2, with an H_2O_2 production efficiency of 54%. Unidirectional carbon fiber cathode produced 7.5 mM of H_2O_2 (96% of H_2O_2 production efficiency) when a voltage of 1.8 V was applied during 180 min to a total area of 480 cm^2 of this material. Acid Orange 7 (AO7) was degraded to a concentration of 0.16 mM during the first 40 min of the process, which represented 95% of the initial concentration. Electrolysis process removed nearly 100% of the AO7 using both cathodes at the end of these experiments (180 min).

1. Introduction

The development of new materials, as well as new applications to the existing ones, has grown exponentially in the last decades. Advanced Oxidation Processes (AOPs) are no exception because the design and the selection of materials are essential in the performance and efficiency of these processes.

AOPs are capable of degrading recalcitrant toxic pollutants, which are not possible to eliminate through other treatment methods. These advanced processes are based on the generation of a highly reactive species (hydroxyl radicals, HO•), which oxidize the organic pollutant (Asghar et al., 2015). AOPs for wastewater treatment include the chemical oxidation, ultraviolet radiation combined with ozone (O_3), hydrogen peroxide (H_2O_2), titanium dioxide (TiO_2), ultrasound-based processes, among others; however remarkable oxidation processes that stand out for their good efficiency results are those based on the Fenton reaction. This process is based on the reaction of H_2O_2 with iron ions (see Eq. (1) and Eq. (2)) (Babuponnusami and Muthukumar, 2014).

$$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + OH^{\bullet} + OH^- \quad (1)$$

$$H_2O_2 + Fe^{3+} \rightarrow Fe^{2+} + H^+ + HO_2^{\cdot} \quad (2)$$

This reaction shows great advantages, as the H_2O_2 is an eco-friendly oxidizer, the iron is abundant and it is one of the least toxic heavy metals. The reaction can be carried out without large and costly technical requirements. However, some of the main disadvantages of this treatment are the industrial production, storage, and transportation of the H_2O_2 (Petrucci et al., 2016).

An attractive approach to eliminate this associated risk is the generation of H_2O_2 in an electrochemical reactor through the reduction of oxygen (O_2) (see equation (3)), that can be activated then with Fe^{2+} ions. This process is known as electro-Fenton (EF) (Moreira et al., 2017). The process has proven to be very useful in the removal of recalcitrant pollutants such as dyes, pharmaceuticals, pesticides, hydrocarbons, among others (Abdessalem et al., 2010; Ozcan et al., 2016; Scialdone et al., 2014; Yavuz et al., 2010).

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$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \tag{3}$$

However, the application of this method has a drawback: the selection of materials for the design of the electrochemical cell electrodes. Material researches are mainly focused on the improvement and development of materials for application in industries such as aerospace, energy, electronics, medical care, and others (Park, 2015). Studies directed to design and improve materials focused on the production of H_2O_2 are scarce. Therefore, researchers engaged in the production of H_2O_2 electrochemically have to deal with the evaluation and optimization of commercial materials for carrying out EF processes (Divyapriya et al., 2017; Mousset et al., 2016; Xia et al., 2015).

Different materials have been used for this purpose, such as platinum, mercury and stainless steel. More complex electrodes, such as Boron-Doped Diamond (BDD) are also used. However, the most widely material used in EF process is carbon (Nidheesh and Gandhimathi, 2012). The use of carbon is attractive due to the characteristics of this material: it is cheap, has large surface area, is inert, and presents good conduction of the electrical current. The graphite, sponges and carbon fibers, the reticulated vitreous carbon, are just some examples that have been used in these processes to produce H_2O_2 (Rosales et al., 2009; Scialdone et al., 2014; Xia et al., 2015). The reduction of O_2 by a carbon electrode can occur through two ways, due to the fact that the O_2 can take 2 or 4 electrons (Li et al., 2015). In the first case, the H_2O_2 is produced as shown in Equation (3). In the second case, the electrochemical reaction forms H_2O (Equation (4)). In addition, if the over potential value in the electrochemical cell is high, the reduction of protons (H^+) could occur to form hydrogen (H_2) (Safizadeh et al., 2016; Xia et al., 2015), (Equations (5) and (6)).

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \tag{4}$$

$$2H^+ + 2e^- \rightarrow H_2 \tag{5}$$

$$H_2\,O_2 + H_2 \rightarrow 2H_2O \tag{6}$$

The formation of H_2O and H_2 are considered undesirable reactions in the H_2O_2 production process. However, these reactions could take place simultaneously and they are almost impossible to remove. Hence, both the electric current consumed and the efficiency of the reaction shown in Equation (2) are important parameters to assess in this process. This evaluation can be done by applying Faraday's law, which allows the calculation of the number of H_2O_2 moles produced as a function of the electric current consumed in the electrolysis (Equation (7)).

$$\mathrm{m}_{\mathrm{H_2O_2}} = \frac{\mathrm{I_c} * \mathrm{t}}{\mathrm{n} * \mathrm{F}} * \varnothing \tag{7}$$

where $\mathrm{m}_{\mathrm{H_2O_2}}$ are the moles of H_2O_2 electroproduced in the cathode surface (m), $\mathrm{I_c}$ represents the electric current (Amps) observed during the electrolysis, t is time of electrolysis process (seconds), n number of electrons transferred, F Faraday constant (96485 C mol^{-1}) and $\varnothing$ electricity efficiency with respect to the production of H_2O_2.

In addition to the type of material used for the construction of the cathode of the electrochemical reactor, it is important to take into account the shape and geometric disposition of this material. Three dimensional porous electrodes, such as RVC, carbon felt, carbon fiber, carbon sponge or carbon nanotubes, are preferred over the two-dimensional materials, such as graphite. The main advantage of three dimensional electrodes is its high specific area, which directly influences in acceptable densities of electrical currents (Bustos-Terrones et al., 2015).

The RVC has been widely used as cathode in the electro-Fenton process for the degradation of dyes (Ghoneim et al., 2011; Vasconcelos et al., 2016). But few studies are presented in literature that use a cathode made of a Unidirectional Carbon Fiber (CF) for producing H_2O_2 (Ramírez et al., 2016). The novelty of this work focuses on the comparison of these two materials (RVC and CF) as cathodes of an electrochemical reactor for producing H_2O_2 to oxidize AO7. An electrochemical cell of parallel plates was designed and constructed specially for this study. H_2O_2 production and AO7 removal efficiencies are compared and the organic matter degradation kinetics is described. A cost analysis is also presented based on energy consumption of both processes.

2. Material and methods

2.1. Electrochemical system

In this study, a particular prototype of a parallel plate reactor was constructed. This kind of electrochemical reactor presents many advantages, such as: ease of construction and assembly, variety of using manufacturing materials, uniform distribution of electric potential, ease of operation, versatile configuration of electrodes options, simple electrical connections and a better control of mass transport. The electrochemical reactor built for this study was composed of four blocks of acrylic (Fig. 1). Among them, rubber gaskets were placed to seal tightly and prevent leakage. Blocks of acrylic (12 × 26 × 1 cm) were assembled with screws.

The electrochemical reactor was divided into two compartments on which the cathode and the anode were placed. In these compartments, the following solutions were used: a catholyte solution was prepared by using H_2SO_4 (0.01 M) and Na_2SO_4 (0.05 M). The anolyte consisted of a solution of H_2SO_4 (0.8M). Fe_2SO_4 (1 mM) was used as a catalyst. Both compartments were separated by a membrane (Nafion® 117) in order to prevent the mixing of the anolyte and catholyte fluids, but to allow the flow of cations. The protons of the anolyte, due to its high concentration, migrate to the catholyte compartment through the surface of the membrane. Anolyte and catholyte fluids remained in circulation by using magnet pumps (Iwaki Magnet Pump MD-10L).

These containers of 1.5 L capacity were coupled to a hydraulic circuit. The connections of the circuit components were joined with hoses and valves. The electrolysis was carried out using a potentiostat connected to the electrochemical reactor. A potential difference was applied to the electrochemical reactor to start the electrolysis. During the electrolysis, oxygen was dosed in the section of the catholyte to keep this solution saturated with it and generate the H_2O_2. The production of H_2O_2 was carried out by passing the electrolyte saturated with the gas through the three-dimensional electrode. The dissolved oxygen takes the available electrons on the surface of the electrode to produce H_2O_2.

2.2. Electrodes design

The electrochemical cell consisted of two electrodes, a cathode and an anode (Sonawane et al., 2017). A stainless steel mesh (SS 304) was used as the anode. The size of the anode was 10.5 × 6.5 cm (with a tab inclined to connect it to the power source). The anode was placed between the plates, close to the membrane and the cathode. In this study, two different carbon cathodes were used: Reticulated Vitreous Carbon and Carbon Fiber. The main objective of the use of these cathodes for the production of H_2O_2 in an electrochemical reactor is the obtaining of the Fenton reagent *in situ*, for the degradation of organic pollutants that are toxic, specifically wastewater from the textile industry. The efficiency for